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**High-Performance 0-3 Type Niobate-based Lead-free Piezoelectric Composite
Ceramics with ZnO Inclusions**

Xiang Lv,^{1,#} Jun Li,^{2,#} Tian-Lu Men,³ Jiagang Wu,^{1*} Xi-xiang Zhang,^{2*} Ke Wang,^{3*}
Jing-Feng Li,³ Dingquan Xiao,¹ and Jianguo Zhu¹

¹*Department of Materials Science, Sichuan University, 610064, Chengdu, P. R. China*

²*King Abdullah University of Science and Technology (KAUST), Division of Physical
Science and Engineering (PSE), Thuwal 23955-6900, Saudi Arabia*

³*State Key Laboratory of New Ceramics and Fine Processing, School of Materials
Science and Engineering, Tsinghua University, 100084, Beijing, P. R. China*

#Equal contribution

*Corresponding author:

E-mail:

wujiagang0208@163.com and msewujg@scu.edu.cn

xixiang.zhang@kaust.edu.sa

wang-ke@tsinghua.edu.cn

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ABSTRACT: Because of their high toxicity, lead-based materials in electronic devices must be replaced by lead-free piezoelectric materials. However, some issues remain that hinder the industrial applications of these alternative ceramics. Here, we report the construction of a 0-3-type ceramic composite (KNNS-BNKZ: x ZnO), where the Sb-doped ZnO sub-micronic particles were randomly distributed throughout the potassium-sodium niobate-based ceramic matrix. In this KNN-based ceramic composite, superior temperature stability, excellent piezoelectric properties, and a high Curie temperature were simultaneously achieved. The unipolar strain varied from +20% to -16% when the temperature was increased from 23 °C to 200 °C in KNNS-BNKZ: x ZnO with $x=0.75$. By increasing the ZnO content from $x=0$ to 5.0, the Curie temperature was increased from 227 °C to 294 °C. More importantly, the piezoelectric coefficient remained high ($d_{33}=480$ -510 pC/N) for a wide range of compositions, $x=0.25$ -1.0. Transmission electron microscopy (TEM) experiments showed that the compensatory electric fields generated by the Sb-doped ZnO sub-micronic particles were responsible for the improved temperature stability. The high piezoelectricity was due to the existence of nanodomains, which were clearly observed in the TEM experiments. The results presented in this work clarify some of the physical mechanisms in this KNN-based ceramic composite, thus advancing the development of lead-free ceramics.

1. INTRODUCTION

Lead-free piezoceramics based on potassium-sodium niobate, i.e., (K,Na)NbO₃ or “KNN”, are considered one of the most promising materials to replace the lead-based ceramics widely used in electronic devices. They have been extensively studied for more than five decades.¹⁻⁶ In 2004, a large piezoelectric coefficient (d_{33}) of ~416

pC/N was observed in highly textured (K,Na,Li)(Nb,Ta,Sb)O₃ ceramics fabricated by the reactive-templated grain growth (RTGG) method.⁶ However, the RTGG method is not suitable for industrial applications owing to the complicated fabrication process and high cost.⁶ Ten years later, our group reported a giant d_{33} in KNN-based ceramics synthesized using the conventional solid-state method.^{7,8} This strong piezoelectric effect was mainly attributed to the appearance of a new phase boundary, the R-T phase boundary. Recently, an ultrahigh d_{33} of 700 pC/N was reported in highly textured KNNS-CZ-BKH ceramics with coexisting rhombohedral (R) and orthorhombic (O) phases.⁹ Although these pronounced properties have been successfully obtained in lead-free KNN-based piezoceramics, some tough issues remain that hinder their industrial applications.⁵ One of the main issues is the strong temperature dependence of their piezoelectric properties, which is an intrinsic drawback of materials with polymorphic phase transition (PPT).^{2,4,5} A weak temperature stability was observed in KNN-based ceramics compared with the common lead-based material Pb(Zr,Ti)O₃ (PZT), whose properties are almost temperature independent along morphotropic phase boundary (MPB).^{1,4,5} In addition, a significant tradeoff between the piezoelectricity and Curie temperature (T_c) has been widely reported in KNN-based and other lead-free piezoelectric ceramics,^{2,4,6,10} indicating that the enhanced piezoelectricity in KNN-based ceramics comes at the cost of reducing their T_c values that determine the maximum operation temperature in applications.^{2,10,11} Therefore, a better understanding of the physical mechanisms ceramics will pave the way to simultaneously enhanced temperature stability, large d_{33} , and high T_c in KNN-based ceramics.

The poor temperature stability of KNN-based ceramics is attributed to PPT (e.g., an

orthorhombic-tetragonal (O-T) phase transition).^{2,4} Significant efforts have been dedicated to addressing this issue; for example, attempts were made to lower the O-T phase transition temperature (T_{O-T}) to below room temperature and to synthesize highly textured KNN-based ceramics or single crystals.^{2,7,12-16} Unfortunately, the former failed to have good piezoelectricity (e.g., $d_{33} < 300$ pC/N) and the latter is too expensive for industrial applications.^{7,12,13,15,16} Recently, composite designs of lead-free ceramics were proposed with both greater temperature stability and enhanced electrical properties.¹⁷⁻²¹ For example, ferroelectric/relaxor composite ceramics consisting of a nonergodic relaxor (0.93BNT-0.07BT) and an ergodic relaxor (0.92BNT-0.06BT-0.02KNN) showed a low critical electric field required for inducing giant strain and a considerably low strain hysteresis, which was interpreted with a model based on two serially-connected capacitors.^{17,18}

ZnO semiconductor, possessing a polarity and piezoelectricity, was widely used to modify the piezoceramics' microstructure and electrical properties, which acted as a sintering aid, substitution additive and composite ceramics' enhancer.^{19,20-22} Particularly, the recent studies showed that composites comprised of lead-free piezoceramics and ZnO semiconductor significantly outperformed other lead-free piezoelectric ceramics in terms of temperature stability.²⁰⁻²² For instance, the depolarization temperature (T_d) of 0.94Bi_{0.5}Na_{0.5}TiO₃-0.06BaTiO₃:*x*ZnO (0.94BNT-6BT:*x*ZnO) ceramic composites increased with increasing ZnO and disappeared at 30 mol% ZnO, greatly improving the temperature stability.²¹ A compensatory polarization electric field induced by the ZnO sub-micronic particles was deemed the origin of the improved temperature stability.²¹ In addition, the thermal stability of a pure KNN ceramic was improved by adding ZnO sub-micronic

particles to form KNN:ZnO composites.²² Although these composites generally exhibited inferior piezoelectricity (e.g., d_{33} <300 pC/N) to lead-based ceramics, the composite design was an effective way to improve their temperature stability and piezoelectricity compared to other lead-free piezoceramics.^{21,22} Charged *n*- or *p*-doped ZnO particles have a much higher density of charge carriers than charged ZnO sub-micronic particles.^{21,22} Therefore, we expect a much better piezoelectricity and higher thermal stability in composites of high-performance KNN-based ceramics and *n*- or *p*-doped ZnO particles.

In this work, we report the fabrication of 0-3-type ceramic composites, denoted by KNNS-BNKZ: x ZnO, in which the ceramic matrix and additive were $0.96(\text{K}_{0.44}\text{Na}_{0.56})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{O}_3$ - $0.04\text{Bi}_{0.5}(\text{Na}_{0.18}\text{K}_{0.82})_{0.5}\text{ZrO}_3$ ceramics and ZnO sub-micronic particles, respectively. These ceramic composites exhibited the following merits: (i) superior temperature stability (the unipolar strain varied from +20% to -16% at 23 °C-200 °C) in KNNS-BNKZ: x ZnO with $x=0.75$; (ii) excellent piezoelectric properties ($d_{33}=480$ -510 pC/N at $x=0.25$ -1.0); (iii) increased T_C from 227 °C to 294 °C at $x=0$ -5.0). We also propose a physical mechanism behind the improved thermal stability.

2. EXPERIMENTAL PRECEDURE

Ceramic composites containing $0.96(\text{K}_{0.44}\text{Na}_{0.56})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{O}_3$ - $0.04\text{Bi}_{0.5}(\text{Na}_{0.18}\text{K}_{0.82})_{0.5}\text{ZrO}_3$ - $x\text{wt}\%\text{ZnO}$, denoted by KNNS-BNKZ: x ZnO, $x=0.25$ -5.0, were prepared by the conventional solid-state method with a two-step method. The raw materials were K_2CO_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Bi_2O_3 (99.999%), Sb_2O_3 (99.99%), and ZrO_2 (99%) (Sinopharm Chemical Reagent Co., Ltd, CN).

Wurtzite structural ZnO powder (99.9%) was bought from Sigma-Aldrich company (USA), with average size less than 5 μm . The detailed preparation process of ceramic composites and related measurements were clearly described in Supporting Information.

3. RESULTS AND DISCUSSION

3.1 Identification of KNNS-BNKZ: $x\text{ZnO}$ ceramic composite

Here, we present evidence of the structure of the KNNS-BNKZ: $x\text{ZnO}$ ceramic composite [Figs. 1-3]. Composition-dependent XRD patterns exhibited that a secondary phase was detected in the samples with $x \geq 0.50$ [see Figure S2 in Supporting Information]. The areas marked by white circles in Figs. 1(a) and (b) show the random distribution of ZnO in the KNNS-BNKK ceramic matrix, which was confirmed by element mappings [Fig. 1(b)]. The enlargement of red dots in Fig. 1(b) shows that the sizes of particles are about 200 nm [Fig. 1(c)]. We performed selected area electron diffraction (SAED) measurement on one randomly chosen particle, and the obtained diffraction pattern along the [001] zone axis was consistent with the wurtzite phase structure, indicating that the ZnO phase is dominant. The similar distribution of ZnO particles was also found in the ceramic composites with $x=5.0$ [see Figure S5 in Supporting Information].

In order to further investigate the chemical composition of the black area indicated by a red circle in Fig. 1(c), we checked the chemical distribution [Fig. 2]. We found considerable concentrations of both the Zn and Sb elements, and some O element. All the other elements were absent, indicating that the black area contained just Zn, O, and Sb. The similar observation was also found in the ceramic composites with $x=5.0$

[see Figure S6 in Supporting Information]. In previous studies, a *p*-type ZnO semiconductor was fabricated by doping ZnO with Sb, after which both the XRD data and SAED patterns of the Sb-doped ZnO remained nearly unchanged.²³⁻²⁵ Additionally, the elemental distributions of the ceramic matrix near the ZnO particles also reflected that Sb replaced Zn [see Figures S4, S7 and Table S1 in Supporting Information]. Therefore, it can be concluded that the secondary phase should be Sb-doped *p*-type ZnO sub-micronic particles.²³⁻²⁶ In accordance with those results, we successfully fabricated 0-3-type ceramic composites comprised of Sb-doped *p*-type ZnO sub-micronic particles and a KNNS-BNKZ ceramic matrix, where the Sb-doped *p*-type ZnO sub-micronic particles were randomly embedded inside the KNNS-BNKZ ceramic matrix.

Figure 1. Structure of the KNNS-BNKZ: x ZnO ceramic composite. (a) Morphology and (b) Electron energy loss spectroscopy (EDS) mapping of Zn in KNNS-BNKZ: x ZnO with $x=0.75$. (c) ZnO particle in the KNNS-BNKZ ceramic matrix. (d) Selected area electron diffraction (SAED) pattern along the $[001]$ zone axis of the ZnO particle shown in (c).

Figure 2. (a) ZnO particle corresponding to the dark spot in Fig. 1(c). Electron energy loss spectroscopy (EELS) element mapping of (b) Zn and (e) Na elements. (c-d) and (f-i) Electron energy loss spectroscopy (EDS) element mappings for K, Nb, Sb, Bi, Zr, and O elements, respectively. Because the Zn (K) and Na (K) peaks overlapped in EDS, we chose the EELS measurement for the Zn and Na elements.

After identifying the Sb-doped *p*-type ZnO phase, we checked the phase structure of the KNNS-BNKZ ceramic matrix. Given the observed relationship between the crystal structure and the electron diffraction patterns, we utilized convergent beam electron diffraction (CBED) to analyze the variation in the phase structure [Fig. 3].²⁷ Figs. 3(a) and (b) show the CBED patterns of the ceramic composite with $x=0.75$ along the [111] zone axis. The (11-2) mirror plane shown in Fig. 3(a) suggests tetragonal (T) symmetry, and the six mirror planes shown in Fig. 3(b) point to rhombohedral (R) symmetry.^{27,28} Thus, we concluded that an R-T phase coexistence

remained in the ceramic matrix of KNNS-BNKZ: $x\text{ZnO}$ with $x=0.75$, consistent with the previous identification of KNNS-BNKZ ceramics.⁷ We also investigated the phase structure of KNNS-BNKZ: $x\text{ZnO}$ with $x=5.0$ by means of the CBED patterns [Figs. 3(d) and (e)]. The (100) mirror plane shown in Fig. 3(d) suggests tetragonal (T) symmetry and the (110) mirror planes shown in Fig. 3(e) point to rhombohedral (R) symmetry.^{27,28} Therefore, we concluded that an R-T phase coexistence remained in the KNN-BNKZ ceramic matrix regardless of the ZnO content, which was also supported by the XRD patterns and temperature-dependent permittivity curves [see Figures S2, S8, and S9 In Supporting Information]. In addition, the microstructure of ceramic composite and how ZnO distributed in ceramic composite were also appropriately evaluated [see Figures S4, S6 and S10-S13 in Supporting Information].

Figure 3. Convergent beam electron diffraction (CBED) patterns of the ceramic composites with (a-b) $x=0.75$ along the $[111]$ zone axis and (c-d) $x=5.0$ along the $[001]$ zone axis. SAED patterns of the ceramic composites with (c) $x=0.75$ and (f) $x=5.0$. The CBED patterns were obtained from different areas.

3.2 Unipolar strain and its temperature stability

Once the KNNS-BNKZ: x ZnO ceramic composites were successfully constructed, we investigated the effects of the Sb-doped p -type ZnO sub-micronic particles on the KNNS-BNKZ ceramic matrix. Figs. 4(a)-(c) depict the temperature-dependent unipolar strain curves of KNNS-BNKZ: x ZnO with $x=0$, 0.75, and 2.0, respectively. With increasing temperatures, the unipolar strain of KNNS-BNKZ: x ZnO with $x=0$ rapidly reduced, while those of KNNS-BNKZ: x ZnO with $x=0.75$ and 2.0 first increased and then deceased. The observed differences among the responses of the temperature-dependent unipolar strains were ascribed to their different T_{R-T} values.

Generally, the piezoelectric response of KNN-based ceramics improves when the ambient temperature approaches the orthorhombic-tetragonal (O-T) and rhombohedral-tetragonal (R-T) phase transition temperatures.^{29,30} In our study, the T_{R-T} of KNNS-BNKZ: x ZnO with $x=0$ was 27 °C [Fig. S7(b)], while KNNS-BNKZ: x ZnO with $x=0.75$ and 2.0 exhibited T_{R-T} of 42 °C and 58 °C, respectively [Figs. S6(c) and (f)]. Thus, a high unipolar strain value of 0.16% was observed in the $x=0$ composite at 23 °C, which clearly decreased at $T>80$ °C. For the composites with $x=0.75$ and 2.0, unipolar strain values of 0.132% and 0.131% were observed at 23 °C. When the measured temperature approached the phase transition temperatures, the unipolar strain values increased to 0.16% and 0.144% for $x=0.75$ and 2.0, respectively. When the temperature increased further, the unipolar strain decreased. Fig. 4(d) shows the temperature stability of the unipolar strains for the ceramic composites with $x=0$, 0.75, and 2.0. The addition of ZnO improved the temperature stability of the unipolar strain. Without ZnO, the normalized unipolar strain of KNNS-BNKK ceramics rapidly decreased from 100% to 48% as the temperature increased from 23 °C to 200 °C [Fig.

4(d)]. After the construction of KNNS-BNKZ: x ZnO ceramic composites (e.g., $x=0.75$ and 2.0), the unipolar strain first increased and then slightly reduced, resulting in a relatively high normalized strain value of 84% and 73% at $T=200\text{ }^{\circ}\text{C}$ [Fig. 4(d)].

Furthermore, the temperature-dependent unipolar strain of the ceramic composites with $x=0.75$ were investigated under different electric fields [Figs. 4(e-g)]. As we increased the electric fields from 1 kV/mm to 3 kV/mm, all the temperature-dependent unipolar strain curves exhibited similar variations within each electric field, as shown in Fig. 4(b). A comparison of the temperature-dependent unipolar strains measured under different electric fields is depicted in Fig. 4(h). We found that increasing the electric field effectively improved the temperature stability of the unipolar strain in the KNNS-BNKZS: x ZnO ceramic composite with $x=0.75$.

Figure 4. Temperature-dependent unipolar strain curves of KNNS-BNKZ: x ZnO ceramic composites with (a) $x=0$, (b) $x=0.75$, and (c) $x=2.0$, measured at $E=4$ kV/mm.

(d) Comparison among the normalized unipolar strains of KNNS-BNKZ: x ZnO ceramic composites with $x=0$, 0.75, and 2.0. The normalized unipolar strain is represented by $S_{(T)}/S_{(RT)}$, in which $S_{(T)}$ is the unipolar strain at measurement temperature T and RT represents room temperature. Temperature-dependent unipolar strain curves of KNNS-BNKZ: x ZnO with $x=0.75$ under (e) 1 kV/mm, (f) 2 kV/mm, and (g) 3 kV/mm. (h) Normalized unipolar strain of the KNNS-BNKZ: x ZnO with $x=0.75$ under different electric fields.

Since an improved temperature stability is expected to better meet the demands of practical applications,⁵ we compared the temperature stabilities of KNNS-BNKZ: x ZnO with $x=0.75$ and 2.0 to those of several other representative lead-free piezoelectric ceramic systems,^{6,9,31-34} as shown in Fig. 5. It is evident that our results from KNNS-BNKZ: x ZnO with $x=0.75$ and 2.0 are comparable to the best ones observed previously in MnO₂-modified KNN-BLT-BZ ceramics (blue line) and in KNNS-BNKH ceramics (magenta line).^{31,32} More importantly, our results from KNNS-BNK: x ZnO with $x=0.75$ are comparable to those of highly textured KNNS-CZ-BKH ceramics (e.g., KNN-3T, orange line) and even more stable than that of commercial PZT-5H ceramics (pink line).^{9,34} More specifically, the relatively small variations in the unipolar strain between +20% and -16% are observed over a wide temperature range of 23-200 °C in KNNS-BNKZ: x ZnO with $x=0.75$, manifesting a strong candidate for applications in piezoelectric actuators operating at room temperature and up to 200 °C.

Figure 5. Temperature stability of the unipolar strains in several representative lead-free ceramic systems.^{6,9,31-34}

Here we propose a rational physical mechanism behind the improved temperature stability [Fig. 6]. Before applying the electric fields, the Sb-doped *p*-type ZnO sub-micronic particles were randomly embedded within grains of the KNNS-BNKH ceramic matrix [Fig. 6(a)]. After applying an electric field (i.e., poling electric field, poling *E*), the Sb-doped *p*-type ZnO sub-micronic particles will generate a Schottky barrier. And then, Schottky barrier will produce a local electric field (i.e., local *E*) that has a very similar direction to that of poling *E* [Fig. 6(b)]. Subsequently, such a local *E* will reinforce the local polarization of KNNS-BNKH ceramic matrix in the proximity, to some extent [Fig. 6(b)]. Because KNNS-BNKH ceramic matrix is insulating, the Schottky barrier will preserve until the charge could be thermally removed, resulting in the enhanced temperature stability. Therefore, such a local electric field induced by the Schottky barrier of Sb-doped *p*-type ZnO sub-micronic particles stabilized the local polarization of the matrix, thereby improving the temperature stability.

Figure 6. Physical model showing how the Sb-doped *p*-type ZnO sub-micronic particles were distributed inside grains of KNNS-BNKZ ceramic matrix (a) before and (b) after poling. The gray and red circles represent charged Sb-doped *p*-type ZnO sub-micronic particles. The red halves possessed positive charges, while the gray halves possessed negative charges.

3.3 d_{33} vs. T_c and domain structures

Consequently, we also investigated the effects of the *p*-type ZnO sub-micronic particles on the piezoelectric properties of the ceramic composites. According to previous studies,¹⁻¹⁰ there is a tradeoff between the d_{33} and T_c of a piezoelectric ceramic material [Fig. 7(b)], in that an increase in T_c is usually accompanied by a decrease in d_{33} , and vice versa. Thus, the enhancement of d_{33} will usually undermine the corresponding T_c , resulting in the unbalanced development of d_{33} and T_c in lead-free piezoelectric ceramic systems [Fig. 7(b)]. However, we were able to realize both high d_{33} (480-510 pC/N) [Fig. 7(a)] and T_c (227-263 °C) [see Figure S9 in

Supporting Information] in the KNNS-BNKZ: x ZnO ceramic composites. Therefore, the piezoelectric properties of the KNNS-BNKZ: x ZnO ceramic composites fill the gap in the development of d_{33} and T_c in lead-free piezoelectric ceramic systems [Fig. 7(b)].

To explain the evolutions of d_{33} and T_c , both tetragonality ratio (c/a) and content of T phase are considered [Fig. 7(a)]. With increasing ZnO content ($x=0-0.75$), d_{33} slightly increases while T_c rapidly increases with a ratio of $36.3\text{ }^{\circ}\text{C}/(1\text{wt}\%)$. Meanwhile, tetragonality ratio (c/a) firstly reduces at $x=0-0.5$ and then increases at $x=0.5-0.75$, whereas the contrary variation is observed in the content of T phase. It was reported that both tetragonality ratio (c/a) and content of T phase affected the piezoelectricity of both Pb-based and Pb-free piezoceramics.³⁵⁻³⁷ Specifically, the larger piezoelectricity can be observed in the ceramics with higher tetragonality ratio (c/a) and more content of T phase, owing to the close relationship between local structure and piezoelectricity.³⁵⁻³⁷ Therefore, the reduced tetragonality ratio (c/a) can be compensated by the increasing content of T phase, resulting in the slightly increased d_{33} at $x=0-0.75$. As x exceeds 0.75, d_{33} reduces continuously while T_c increases at a lower speed of $9.67\text{ }^{\circ}\text{C}/(1\text{wt}\%)$. Here, the reduced d_{33} mainly originates from the both decreasing tetragonality ratio (c/a) and content of T phase at $x\geq 0.75$. The increased T_c may be stem from the occupation of A-site by Zn^{2+} , which was also observed in ZnO-doped KNL-NTS ceramics.³⁵ It should be pointed out that such a replacement has a limitation, resulting in a critical point at $x=1.0$ beside which two different increasing rates of T_c were observed.³⁵

Figure 7. (a) Variations of T_c , d_{33} , tetragonality ratio (c/a) and content of T phase in this work as a function of ZnO content (d_{33} and T_c values of the ceramics with $x=0$ were extracted from Ref. 7). The size of error bars is slightly smaller than that of data symbols. (b) Relationship between d_{33} and T_c (or T_d) in typical perovskite lead-free piezoceramics. T_d is the depolarization temperature of BNT-based ceramics, above which d_{33} of BNT-based ceramics disappears.

As we mentioned above, the domain structures provide an extrinsic contribution to the piezoelectricity of piezoelectric materials. Therefore, it is interesting to explore correlation between the domain structures and d_{33} in this ceramic composite. Fig. 8 shows the TEM images of the samples with $x=0.75$ and 5.0. For the ceramic composite with $x=0.75$, complex domain structures were observed, including the lamellar type (solid line ellipse), arrow type (dotted arrows), and watermark type (dotted ellipses) [Fig. 8(a)]. The watermark and arrow types are characteristic of 180°

and 90° domains, respectively.³⁸ Lamellar domains were previously observed in Pb-based and Pb-free materials with exceptional piezoelectric properties.^{39,40} We observed submicron-domain structures with stripes at the 200 nm scale within the ellipse in Fig. 8(a), as indicated by the white solid line. The figure shows that the submicron-domain structure was constructed from nanodomains ~20 nm across and in a hierarchical distribution that was regarded in past reports as the origin of the piezoelectric properties in Pb-based and Pb-free piezoceramics.^{39,40} Fig. 8(b) shows the domain structure of the ceramic composite with $x=5.0$. Compared with that of $x=0.75$, fewer ferroelectric domains were observed, indicating a reduction in the quantity of ferroelectric domains due to the high ZnO content, and then led to the degraded piezoelectricity. Here, it should be pointed out that domains that are determined by TEM are typically smaller than the real domain of the single crystal and ceramics because the thickness of TEM preparation is smaller than that of the grain size of ceramic composites.^{9,32} However, the obvious contrast of domain structure regarding quantity and size are observed in the ceramic composites with $x=0.75$ and 5.0 [Fig. 8], which is enough to explain their piezoelectric differences.

It is well established that $d \propto \sqrt{a}$, where d is the domain width and a is the grain size.^{41,42} In principle, a smaller domain configuration is highly anticipated in ceramic composites with high ZnO content (e. g., $x \geq 2.0$) due to decreased grains [see Figure S10 in Supporting Information]. However, the low T phase content, small tetragonality (c/a) and substantial deviation from stoichiometric ratio result in the diminishing domain configurations. On the contrary, the ceramic composites with $0.25 \leq x < 2.0$ possess the decent grain size, high T phase content and large tetragonality (c/a) due to the reservation of stoichiometric ratio as much as possible. Such a grain

size brings in two effects. On the one hand, the slightly increased grain size will generate the larger domain structure, leading to the occurrence of more hierarchies that contain more nano-domains.^{39,40} On the other hand, the enhanced domain switching and reduced residual stress are achieved owing to the slightly increased grain size.⁴³ Considering the easy switching of nano-domains under an applied electric field, both effects, therefore, can promote the piezoelectric properties.³⁸⁻⁴³ While, diminishing domain structures, low T phase content and small tetragonality (c/a), which are induced by the deviation from the stoichiometric ratio, are responsible for the moderate piezoelectricity (d_{33} =210-310 pC/N) in the ceramic composite with $x \geq 3.0\%$.

Figure 8. Domain structures of KNNS-BNKZ: x ZnO ceramic composites with (a) $x=0.75$ and (b) $x=5.0$.

4. CONCLUSIONS

We achieved superior temperature stability, excellent piezoelectric properties (large d_{33} values of 480-510 pC/N), and increased T_c (227-294 °C) simultaneously in our KNNS-BNKZ: x ZnO ceramic composites. Using the conventional solid-state reaction method, we synthesized these 0-3-type ceramic composites from Sb-doped p -type

ZnO sub-micronic particles and a KNNS-BNKZ ceramic matrix. Thus, the unipolar strain of the ceramic composite with $x=0.75$ varied from +20% to -16% at 23 °C–200 °C due to the compensatory electric field originating from the Schottky barrier that occurred near Sb-doped *p*-type ZnO sub-micronic particles regions.

But even more importantly, we identified the nanodomain structures and multiphase coexistence as the origins of the high piezoelectric response via TEM. Clear images of the ceramic composite structure were obtained from the HR-TEM and CBED patterns. Sb-doped *p*-type ZnO sub-micronic particles were clearly identified by the SAED pattern, which presented a wurtzite phase structure, and the CBED patterns revealed the R-T phase coexistence in the KNNS-BNKK ceramic matrix. Due to the R-T phase coexistence, the ferroelectric domain structures had shrunk down to the nanoscale. The nanodomains were self-assembled into submicron-domain structures with a hierarchical configuration. These nanodomain structures with scale of ~20 nm, high T phase content, and large tetragonality (c/a) generated the high piezoelectric properties.

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